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**Process for manufacturing a catalyst-coated polymer electrolyte membrane****Description**

10 The invention relates to a process for manufacturing a catalyst-coated polymer electrolyte membrane ("CCM") for electrochemical devices such as, e.g., fuel cells, electrochemical sensors or electrolyzers. Furthermore, the present invention embraces the use of those catalyst-coated membranes for manufacture of membrane electrode assemblies (MEAs) and fuel cell stacks.

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Fuel cells convert a fuel and an oxidising agent into electricity, heat and water at two spatially separated electrodes. Hydrogen, methanol or a hydrogen-rich gas can be used as the fuel and oxygen or air as the oxidising agent. The energy conversion process in the fuel cell is distinguished by particularly high efficiency. For this reason, fuel cells are gaining increasing importance for alternative propulsion concepts, stationary power supply systems and portable applications.

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Due to their low operation temperature, their compact structure and their power density, membrane fuel cells, e.g. the polymer electrolyte membrane fuel cell ("PEMFC") and the direct methanol fuel cell ("DMFC"), are suitable for a wide range of mobile and stationary applications.

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PEM fuel cells are built by stacking a plurality of fuel cell units. The individual units are electrically connected in series in order to increase the operating cell voltage.

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The main part of a PEM fuel cell is the so-called membrane-electrode-assembly (MEA). The MEA comprises a proton-conducting membrane (polymer electrolyte or ionomer membrane), two gas diffusion layers (GDLs) arranged at the sides of the membrane and the electrode layers arranged between the membrane and the respective gas diffusion layer. One of the electrode layers serves as anode for the oxidation of water and the second electrode layer serves as cathode for the reduction of oxygen.

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The polymer electrolyte membrane consists of proton-conducting polymer materials. This materials are shortly called "ionomers" hereinafter. A tetrafluoroethylene-fluorovinylether-copolymer having sulfonic acid groups is preferably used. This material is available, e.g., under the trademark Nafion® by DuPont. However, other materials, especially fluorine-free ionomer materials like doped sulfonized polyetherketones or doped

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5 sulfonized or sulfinized arylketones or polybenzimidazoles can be used. Suitable ionomer materials are described by O. Savadogo in the "Journal of New Materials for Electrochemical Systems" I, 47-66 (1998). For the use in fuel cells, these membranes generally have a thickness of between 10  $\mu\text{m}$  and 200  $\mu\text{m}$ .

10 The electrode layers for anode and cathode comprise a proton-conducting polymer and electrocatalysts, which catalytically promote the respective reactions (oxidation of hydrogen and reduction of oxygen). The metals of the platinum group of the periodic system of elements are preferably used as catalytically active components. In most cases, so-called supported catalysts are used, in which the catalytically active platinum group metals are  
15 fixed to the surface of a electrically conductive support material, e.g., carbon black, in a highly dispersed form.

The gas diffusion layers (GDLs) usually consist of a carbon fiber paper or carbon fiber cloth and allow a good access of the reactant gases to the reaction layers. Furthermore,  
20 they serve as good conductors for the current generated in the fuel cell and remove the product water formed.

The present invention relates to the manufacturing of 3-layer catalyst-coated membranes (CCMs) by direct coating methods. For manufacturing such catalyst-coated  
25 membranes ("3-layer CCMs") the electrode layers are mostly applied to the front and back side of the polymer electrolyte membrane by printing, doctor-blading, rolling or spraying of a paste. The pasty compositions are also referred to as inks or catalyst inks in the following. Besides the catalyst, they usually contain a proton-conductive material, various solvents as well as optionally finely dispersed hydrophobic materials, additives and pore formers.

30 Commercialization of the PEM fuel cell technology requires industrial-scale production methods for catalyst-coated membranes (CCMs) and membrane-electrode-assemblies (MEAs) in order to make them available in commercial quantities for mobile, stationary and portable applications. The following documents show the state of the art in  
35 this field.

WO 97/23919 describes a method for manufacturing membrane-electrode-assemblies whereby the polymer membrane, the electrode layers and the gas diffusion layers are continuously bonded together by rolling. This method relates to the manufacturing of MEAs  
40 with five layers, a direct coating of the ionomer membrane (CCM production) is not mentioned.

5 EP 1 198 021 discloses a continuous method for manufacturing MEAs having five layers, in which the opposite side of the membrane is supported during application of the catalyst layer. Contrary to the process according to the present invention, the side of the membrane lying opposite to the catalyst layer is supported during printing by a gas diffusion layer (GDL) in tape form (and not by a temporarily applied film). At the end of the process,  
10 the gas diffusion layer in tape form remains as a component of the 5-layer MEA.

EP 1 037 295 describes a continuous process for the selective application of electrode layers onto an ionomer membrane in tape form, in which the front and the back side of the membrane is coated by printing. Here, the membrane must have a specific water content  
15 (from 2 wt.-% to 20 wt.-%). Due to the swelling and the dimensional changes of the membrane during the coating process, the positioning accuracy between the front and backside prints becomes critical, especially when using thin membranes with less than 50  $\mu\text{m}$  thickness.

20 US 6,074,692 describes a continuous method for coating an ionomer membrane. The membrane is pre-swollen in an organic solvent and then coated. The shrinkage of the membrane during the drying process is impeded by clamps.

WO 02/43171 suggests a flexographic printing method in which a thin catalyst layer  
25 is transferred to the membrane by a printing device having the shape of a drum. By applying multiple very thin layers, it is attempted to reduce the swelling of the membrane.

JP 2001 160 405 discloses a process for manufacturing a catalyst-coated ionomer membrane, too. Here, the membrane is fixed to a support substrate which is removed after  
30 the coating of the frontside and the drying thereof. Before coating the backside, the membrane is fixed to a further support substrate. Substrates based on polyester or Teflon as well as glass plates are suggested. The handling of the membrane during the coating of the front and the backside of the membrane is done while the membrane is not supported. Thus, this process is not continuous and not suitable for series production of catalyst-coated  
35 membranes.

The industrial production of 3-layer catalyst-coated membranes (CCMs) still provides problems, which have not been solved by the known measures in a satisfactory manner. Especially, the swelling of the membrane during coating with solvent-based inks,  
40 the shrinkage during the subsequent drying steps as well as the high sensitivity of the membranes during handling and processing present challenges to a suitable continuous manufacturing process.

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Thus, it is the object of the present invention to provide an improved process for manufacture of catalyst-coated polymer electrolyte membranes. This process should overcome the above-indicated disadvantages of the state of the art.

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This object is solved by the process according to claim 1 and a corresponding apparatus. Advantageous embodiments are described in subsequent claims. Further claims are related to the use of catalyst-coated membranes manufactured according to the process of claim 1 for assembling electrochemical devices, e.g., fuel cells, sensors or electrolyzers.

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A particularly preferred process according to the present invention comprises several steps and is characterized in that

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(a) the frontside of a strip-shaped polymer electrolyte membrane, comprising a first supporting foil on its back side, is coated with a catalyst ink and dried at an elevated temperature,

(b) a second supporting foil is applied to the front side of the polymer electrolyte membrane,

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(c) the first supporting foil is removed from the back side of the polymer electrolyte membrane,

(d) subsequently the backside of the polymer electrolyte membrane is coated with a catalyst ink and dried at an elevated temperature.

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The second supporting foil on the front side of the membrane can be removed, if necessary, immediately after the first step or in the course of further processing steps. Further processing steps may embrace, e.g., the post-treatment of the CCM in an aqueous bath, the assembly of the CCM with the gas diffusion layers (GDLs) to form 5-layer MEAs or the bonding of the CCM with protective layers and/or sealing components. Generally, if an improved handling throughout the process is required, the second supporting foil may remain on the polymer electrolyte membrane and may only be removed for the final assembly of the MEA or the fuel cell stack.

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Preferably, strip- or tape-shaped ionomer membranes are used, which are already laminated onto a supporting foil when supplied. In the meantime, various membrane suppliers offer such products. If an unsupported strip-shaped membrane must be used in the

- 5 process according to the present invention, the back side of the membrane is laminated with a first supporting foil in a separate simple process step beforehand.

10 In the first process step (a), a catalyst ink is applied to the front side of the supported membrane. After drying of the catalyst ink, a second supporting foil is applied to the front side of the coated membrane in the second process step (b) and subsequently, in the third process step (c), the first supporting foil on the backside of the membrane is removed. In the present application, the process steps (b) and (c) are, in summary, also referred to as "trans-lamination".

- 15 In a final process step (d), the back side of the membrane is coated and subsequently dried.

20 As already mentioned, the second supporting foil on the front side of the membrane may be removed, if necessary, immediately or in the course of later processing steps.

**Figure 1** shows the procedural flow of the process according to the present invention.

25 A feature of the process according to the present invention is the continuous production flow when using strip-shaped substrates. It should be noted, that the polymer membrane as well as the supporting foil can be used in strip form.

30 A further feature of the process of the present invention is the application of a second supporting foil onto the front side of the membrane prior to the back side is coated in the second coating step. In a preferred embodiment, the second supporting foil is applied before the first supporting foil is removed. Thus, problems occurring during the removal/delamination of the first supporting foil (for example due to uneven stretching, forming of folds, sagging etc.) are avoided.

35 The process according to the present invention is characterized by the fact, that the membrane is in contact or connected with at least one supporting foil during all processing steps. Therefore, the membrane can be processed economically and efficiently (i.e., with high speed and high quality). Thus, smooth, wrinkle-free and accurately printed catalyst-coated membranes (CCMs) are obtained.

40 In a specific embodiment of the process according to the present invention, punched or perforated films are used as supporting foils. Here, the perforation or punching technique has an influence on the lamination properties of the supporting foil. Perforations having the shape of dots or slits can be used. They can be manufactured by punching, stamping, hot-

5 needle or gas-flame perforation methods or also electrostatically. Typical perforation patterns comprise 5 to 20 holes per square centimeter (cm<sup>2</sup>) foil, whereby the holes have a diameter in the range of about 0,2 mm to 3 mm. Under the term "holes", it is referred to all kinds of openings or gaps in the support foil or film, e.g., non-circular punched openings.

10 It has been found, that the ionomer membrane shows considerably less contractions and/or wrinkles if perforated supporting foils are used. Apparently, the solvent can be better removed through the holes or openings during the drying process following the coating. Additionally, the perforated supported foil allows the membrane to swell due to the penetrating solvent to a certain degree after coating and to contract again in the course of the  
15 drying process. The use of perforated supporting foils is particularly advantageous for larger printing formats (i.e., CCMs with an active area greater than 200 cm<sup>2</sup>), in the case of full-area prints and when thin ionomer membranes (thickness less than 50 µm) are used.

Continuous lamination methods using rollers or presses in a wide range of  
20 temperatures or pressures are used for applying the supporting films onto the polymer electrolyte membrane. Depending on the material combination of the films to be processed, no additional components may be necessary for the lamination process. In certain cases, the adhesion forces between the supporting foil and the membrane may already provide sufficient adhesion. If an improved adhesion between supporting foil and membrane is  
25 desired, so-called adhesive materials may be applied to the edges of the coated side of the membrane. Here, liquid adhesives or adhesive tapes can be used. The lamination conditions are accordingly adapted.

The hot needle perforation method can be used to improve the bonding, too. Here, the supporting foil to be bonded and the ionomer membrane are molten in the pricking area  
30 of the hot needle and thus good adhesion is obtained.

Foils or films of polyester, polyethylene, polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinyl chloride (PVC), polycarbonate, polyamide, polyimide, polyurethane or of comparable foil materials are suitable as supporting foils for the front and  
35 the backside. Furthermore, laminated films, e.g., of polyester/polyethylene, polyamide/polyethylene, polyamide/polyester, polyester/paper, polyethylene/aluminum etc. can be used. Furthermore metal foils and paper materials can be used. The foil materials have a thickness range of 10 µm to 250 µm and a dimensional width of up to a maximum of 750 mm.

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Generally, as material for the second supporting foil, the same films and foils as for the first supporting foil can be used.

5            Suitable devices for continuous processing, coating and lamination of tape-shaped films or foils in a roll-to-roll process are known to the person skilled in the art. The coating of the front side and the back side of the ionomer membrane can be achieved by different methods. Examples are, inter alia, screen printing, stencil printing, offset printing, transfer printing, doctor-blading or spraying. These methods are suitable for the processing of  
10   polymer electrolyte membranes comprising of polymeric perfluorinated sulphonic acids compositions, doped polybenzimidazoles, polyether ketones and polysulphones in the acid or the alkaline form. Composite and ceramic membranes can be used, too.

            Suitable continuous drying methods are, inter alia, hot air drying, infrared drying,  
15   micro-wave drying, plasma methods and/or combinations thereof. The drying profile (temperature and time) is selected according to the specific process. Suitable temperatures are in the range of 20 to 150°C, suitable drying times are between 1 and 30 minutes.

            The electrode layers on both side of the ionomer membrane may differ from each  
20   other. They can be made from different catalyst inks and can have different amounts of catalyst and precious metal loadings (in mg Pt/cm<sup>2</sup>). In the inks, different electrocatalysts, e.g., precious metal containing and base metal containing supported catalysts, Pt- or PtRu-catalysts as well as unsupported Pt and PtRu powders and blacks can be used, depending on the type of fuel cell for which the CCMs or MEAs are made.

25            The following examples will explain the process according to the present invention in more detail without limiting the scope of the invention.

### 30   **Example 1:**

            For producing a membrane-electrode-assembly according to the process of the present invention, a catalyst ink having the following composition was used:

#### 35   **Composition of the catalyst ink (anode and cathode):**

15,0 g	Pt-supported catalyst (40 wt.-% Pt on carbon black)
44,0 g	Nafion® solution (11,4 wt.-% in water)
41,0 g	Propylene glycol
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100,0 g	

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            A strip of 30 cm width and 50 m length of a polymer electrolyte membrane (Nafion® 112, DuPont; H<sup>+</sup>-form, 50 µm thickness) which is supported on one surface by a laminated

5 polyester foil (50  $\mu\text{m}$  thickness), is first coated with the catalyst ink by screen printing on the front surface in a continuous roll-to-roll coating device (set-up described in EP 1 037 295). The coated area is 225  $\text{cm}^2$  (dimensions of the active area: 15 x 15 cm). After printing, the catalyst-coated membrane is dried with hot air in a continuous belt dryer and is wound up by a winder.

10 After coating of the first side, a second perforated supporting foil (polyester, perforation pattern 12 holes/ $\text{cm}^2$ , hole diameter 0,5 mm) is laminated onto the coated front side. For this means, the coated membrane is supplied and positioned in a wrinkle-free form to a lamination device (comprising of a roll-to-roll lamination machine with a winding and unwinding unit, driving rolls, etc.). Simultaneously, the second supporting foil is accurately  
15 provided. The bonding of the second supporting film to the membrane is achieved by a heated roller. Subsequently the first supporting foil is removed from the membrane and is wound up.

After the trans-lamination, the membrane is accurately coated on its backside with the same catalyst ink in a single printing process. The drying profile is adjusted to a  
20 maximum temperature of 75°C and a total drying time of 5 min.

Subsequently, the second perforated supporting is removed and the catalyst-coated, strip-shaped ionomer membrane (CCM) is watered in deionized water (DI water) having a temperature of 80°C, subsequently dried and wound up. The CCMs thus produced comprise a total platinum loading of 0,6 mg Pt/ $\text{cm}^2$  in their active area (0,2 mg Pt/ $\text{cm}^2$  on the anode,  
25 0,4 mg Pt/ $\text{cm}^2$  on the cathode).

For electrochemical testing, an active area of 7 x 7 cm (50 $\text{cm}^2$ ) is cut out from a coated membrane area and this CCM is processed to form a 5-layer membrane-electrode-assembly (MEA). Therefore, hydrophobized carbon fiber paper (Toray TGPH-060, 200  $\mu\text{m}$  thickness) is applied on both sides of the CCM, this structure is assembled by hot pressing  
30 and the MEA thus obtained is mounted into a PEMFC single cell. For performance testing, hydrogen ( $\text{H}_2$ ) is used as anode gas and air is used as cathode gas. The cell temperature is 75°C. Humidification of the anode and the cathode is conducted at 75°C. The working gases have a pressure of 1,5 bar (absolute). The cell voltage measured is 720 mV at a current density of 600 mA/ $\text{cm}^2$ . This corresponds to a power density of about 0,43 W/ $\text{cm}^2$ .

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#### Example 2:

A MEA to be used in a direct methanol fuel cell (DMFC) is produced. An extruded  
40 ionomer membrane in strip-form with a thickness of 87,5  $\mu\text{m}$  is used as membrane, to which a first supporting foil of polyester is laminated. The polymer electrolyte membrane is then coated with an anode ink on the front side, the ink having the following composition:

5    **Composition of the anode ink**

	15,0 g	PtRu-supported catalyst (60 wt.% PtRu/C, ref. to US 6,007,934)
	60,0 g	Nafion® solution (10 wt-% in water)
	15,0 g	Water (deionized)
	10,0 g	Propylene glycol
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	100,0 g	

The printing format is 7 x 7 cm (active area 50 cm<sup>2</sup>). After printing, the coated membrane is dried with hot air in a continuous belt dryer and is wound up by a winder.

After the coating of the first side, a second perforated supporting foil (polyester, perforation pattern 12 holes/cm<sup>2</sup>, hole diameter 0,5 mm) is laminated onto the catalyst-coated frontside. Therefore, the membrane is provided in a wrinkle-free form to a lamination unit and accurately positioned. Simultaneously, the second supporting foil is accurately provided. The lamination of the second supporting film with the membrane is achieved by a heated roller. Subsequently, the first supporting foil is removed from the membrane and is wound up.

The coating of the backside of the supported membrane is conducted with the Pt-catalyst ink from example 1 in a single printing process. The drying profile is adjusted to maximum temperature of 75°C and a total drying time of 5 min. Subsequently, the strip-shaped catalyst coated membrane (CCM) with the perforated supporting foil is watered in deionized water having a temperature of 80°C, dried and then wound up. The precious metal loading of the catalyst-coated membrane is 1 mg PtRu/cm<sup>2</sup> on the anode and 0,6 mg Pt/cm<sup>2</sup> on the cathode.

In order to assemble a 5-layer MEA, the perforated second supporting foil is removed, the CCMs are cut into a single units, and two gas diffusion layers (consisting of hydrophobized carbon fiber paper) are applied to the front and back side of each CCM. Subsequently, the assembly is achieved by hot pressing at a temperature of 140°C and a pressure of 60 bar.

The MEAs are tested in a DMFC test station with an active cell area of 50 cm<sup>2</sup>. Air is used as cathode gas. An average power density of 65 mW/cm<sup>2</sup> is obtained (2-molar MeOH solution, cell temperature 60°C).